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<b>(54) Title:</b> LITHOGRAPHIC PRINTING PLATES WITH A SOL-GEL LAYER  <b>(57) Abstract</b>  A lithographic printing plate comprises a support, a melanophilic layer and a surface melanophobic layer, the latter containing cross-linked colloids derived from certain metal oxides. The plates are long-running plates that require no post-imaging processing.		

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**LITHOGRAPHIC PRINTING PLATES WITH A SOL-GEL LAYER**

This invention relates in general to lithographic printing plates and particularly to lithographic printing plates which do not require wet processing.

5           The art of lithographic printing is based upon the immiscibility of oil and water, wherein the oily material or ink is preferentially retained by the image area and the water or fountain solution is preferentially retained by the non-image area. When a suitably prepared surface is moistened with water and an ink is then applied, the background or non-image area retains the water and repels the ink  
10 while the image area accepts the ink and repels the water. The ink on the image area is then transferred to the surface of a material upon which the image is to be reproduced; such as paper, cloth and the like. Commonly the ink is transferred to an intermediate material called the blanket which in turn transfers the ink to the surface of the material upon which the image is to be reproduced.

15           A very widely used type of lithographic printing plate has a light-sensitive coating applied to an aluminum base support. The coating may respond to light by having the portion which is exposed become soluble so that it is removed in the developing process. Such a plate is referred to as positive-working. Conversely, when that portion of the coating which is exposed becomes hardened,  
20 the plate is referred to as negative-working. In both instances the image area remaining is ink-receptive or oleophilic and the non-image area or background is water-receptive or hydrophilic. The differentiation between image and non-image areas is made in the exposure process where a film is applied to the plate with a vacuum to insure good contact. The plate is then exposed to a light source, a  
25 portion of which is composed of UV radiation. In the instance where a positive plate is used, the area on the film that corresponds to the image on the plate is opaque so that no light will strike the plate, whereas the area on the film that corresponds to the non-image area is clear and permits the transmission of light to the coating which then becomes more soluble and is removed. In the case of a  
30 negative plate the converse is true. The area on the film corresponding to the image area is clear while the non-image area is opaque. The coating under the clear area of film is hardened by the action of light while the area not struck by light is removed. The light-hardened surface of a negative plate is therefore oleophilic and will accept ink while the non-image area which has had the coating  
35 removed through the action of a developer is desensitized and is therefore hydrophilic.

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The prior art has tried to produce such plates by a variety of means. All of them fall short of a plate that has high writing sensitivity, high image quality, short roll up, and long run length without any processing.

US-A-5,372,907 describes a direct write litho plate which is  
5 exposed to the laser beam, then heated to crosslink and thereby prevent the development of the exposed areas and to simultaneously render the unexposed areas more developable, and the plate is then developed in conventional alkaline plate developer solution. The problem with this is that developer solutions and the equipment that contains them require maintenance, cleaning, and periodic  
10 developer replenishment, all of which are costly and cumbersome.

US-A-4,034,183 describes a direct write litho plate without development that is a laser absorbing hydrophilic top layer coated on a support is exposed to a laser beam to burn the absorber to convert it from an ink repelling to an ink receiving state. All of the examples and teachings require a high power  
15 laser, and the run lengths of the resulting litho plates are limited.

US-A-3,832,948 describes both a printing plate with a hydrophilic layer that may be ablated by strong light from a hydrophobic support and also a printing plate with a hydrophobic layer that may be ablated from a hydrophilic support. However, no examples are given.

US-A-3,964,389 describes a no process printing plate made by laser  
20 transfer of material from a carrier film (donor) to a lithographic surface. The problem of this method is that small particles of dust trapped between the two layers may cause image degradation. Also, two sheets to prepare is more expensive.

US-A-4,054,094 describes a process for making a litho plate by  
25 using a laser beam to etch away a thin top coating of polysilicic acid on a polyester base, thereby rendering the exposed areas receptive to ink. No details of run length or print quality are given, but it is expected that an uncrosslinked polymer such as polysilicic acid will wear off relatively rapidly and give a short run length of  
30 acceptable prints.

US-A-4,081,572 describes a method for preparing a printing master  
on a substrate by coating the substrate with a hydrophilic polyamic acid and then imagewise converting the polyamic acid to melanophilic polyimide with heat from a flash lamp or a laser. No details of run length, image quality or ink/water balance  
35 are given.

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US-A-4,731,317 describes a method for making a litho plate by coating a polymeric diazo resin on a grained anodized aluminum litho support, exposing the image areas with a YAG laser, and then processing the plate with a graphic arts lacquer. The lacquering step is inconvenient and expensive.

5 Japanese Kokai No. 55/105560 describes a method of preparation of a litho plate by laser beam removal of a hydrophilic layer coated on a melanophilic support, in which the hydrophilic layer contains colloidal silica, colloidal alumina, a carboxylic acid, or a salt of a carboxylic acid. The only  
10 examples given use colloidal alumina alone, or zinc acetate alone, with no crosslinkers or addenda. No details are given for the ink/water balance or limiting run length.

WO 92/09934 describes and broadly claims any photosensitive composition containing a photoacid generator, and a polymer with acid labile tetrahydropyranyl groups. This would include a hydrophobic/hydrophilic switching  
15 lithographic plate composition. However, such a polymeric switch is known to give weak discrimination between ink and water in the printing process.

EP 0 562 952 A1 describes a printing plate having a polymeric azide coated on a lithographic support, and removal of the polymeric azide by exposure to a laser beam. No printing press examples are given.

20 WO 94/18005 describes a printing plate having a laser absorbing layer coated on a support with a crosslinked hydrophilic layer which is removed upon exposure to the laser. All the examples teach a polyvinyl alcohol layer crosslinked with hydrolyzed tetraethylorthosilicate.

US-A-5,460,918 describes a thermal transfer process for preparing  
25 a litho plate from a donor with an oxazoline polymer to a silicate surface receiver. A two sheet system such as this is subject to image quality problems from dust and the expense of preparing two sheets.

It would be desirable to have a litho plate that has high writing sensitivity, high image quality, short roll up, and long run length without any post-  
30 imaging processing. None of the prior art examples can do this satisfactorily.

The present invention is a lithographic printing plate in which a support web is coated with an ink accepting laser absorbing layer which is subsequently overcoated with a crosslinked hydrophilic layer having metal oxide groups on the surface. Exposure of this plate to a high intensity laser beam  
35 followed by mounting on a press results in excellent impressions without post-imaging processing.

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The lithographic printing plate comprises:

- a) a support web, and
- b) a coextensive melanophilic photothermal conversion layer ,

the printing plate characterized as further comprising a coextensive  
5 melanophobic layer comprising a crosslinked polymeric matrix containing a colloid  
of beryllium, magnesium, aluminum, silicon, gadolinium, germanium, arsenic,  
indium, tin, antimony, tellurium, lead, bismuth or a transition metal oxide.

The support for this invention can be a polymer, metal or paper foil,  
or a lamination of any of the three. The thickness of the support can be varied, as  
10 long as it is sufficient to sustain the wear of the printing press and thin enough to  
wrap around the printing form. A preferred embodiment uses polyethylene  
terephthalate in a thickness from 100 to 200  $\mu\text{m}$ . Another preferred embodiment  
uses aluminum from 100 to 500  $\mu\text{m}$  in thickness. The support should resist  
stretching so the color printing records will register in a full color image. The  
15 support may be coated with one or more "subbing" layers to improve adhesion of  
the final assemblage. The back side of the support may be coated with antistat  
agents and/or slipping layers or matte layers to improve handling and "feel" of the  
litho plate.

The term "melanophilic" is Greek for ink-loving or ink accepting.  
20 Since most conventional printing inks are linseed oil based, melanophilic will  
usually coincide with oleophilic. "Melanophobic" refers to ink-repelling or water-  
loving.

The photothermal conversion layer absorbs laser radiation and  
converts it into heat. It converts photons into phonons. To do this it must contain  
25 a non-luminescent absorber. Such an absorber may be a dye, a pigment, a metal, or  
a dichroic stack of materials that absorb by virtue of their refractive index and  
thickness. The absorber may be in the hydrophilic layer or thermally close to the  
hydrophilic layer. By this it is implied that a significant portion of the heat  
generated by the absorber acts to raise the temperature of the hydrophilic layer to a  
30 level where switching to the melanophilic state occurs. Examples of dyes useful as  
absorbers for near infrared diode laser beams may be found in US-A-4,973,572. A  
useful pigment is carbon.

The binder used to hold the dye or pigment in the photothermal  
conversion layer may be chosen from a large list of film forming polymers. Useful  
35 polymers may be found in the families of polycarbonates, polyesters, and  
polyacrylates. Chemically modified cellulosic binders are particularly useful, such

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as nitrocellulose, cellulose acetate propionate, and cellulose acetate. Exemplary polymers may be found in US-A-4,695,286; US-A-4,470,797; US-A-4,775,657; and US-A-4,962,081.

5 Surfactants may be included in the photothermal conversion layer to facilitate coating uniformity. A particularly useful surfactant for solvent coated polymer layers is DC510, a silicone oil sold by the Dow Corning Company of Midland, Michigan.

10 The melanophobic layer is intended to be wet effectively by an aqueous fountain solution in the lithographic printing process, and when wet, to repel the ink. In addition it is useful if the hydrophilic layer is somewhat porous, so that wetting is even more effective. The hydrophilic layer must be crosslinked if long printing run lengths are to be achieved, because an uncrosslinked layer will wear away too quickly. Many crosslinked hydrophilic layers are available. Those derived from di-, tri-, or tetraalkoxy silanes or titanates, zirconates and aluminates  
15 are particularly useful in this invention. Examples are colloids of hydroxysilicon, hydroxyaluminum, hydroxytitanium and hydroxyzirconium. These colloids are formed by methods fully described in US-A-2,244,325; US-A-2,574,902; and US-A-2,597,872. Stable dispersions of such colloids can be conveniently purchased from companies such as the DuPont Company of Wilmington, Delaware. The  
20 hydrophilic layer is most effective when it contains a minimum amount of hydrophobic groups such as methyl or alkyl groups. The hydrophilic layer preferably should contain less than 5% hydrocarbon groups by weight. A preferred embodiment of the invention uses aminopropyltriethoxysilane as the crosslinking and polymer forming layer, with the addition of colloidal silica to add porosity to the layer. The thickness of the crosslinking and polymer forming layer may be  
25 from 0.05 to 1  $\mu\text{m}$  in thickness, and most preferably from 0.1 to 0.3  $\mu\text{m}$  in thickness. The amount of silica added to the layer may be from 100 to 5000% of the crosslinking agent, and most preferably from 500% to 1500% of the crosslinking agent. Surfactants, dyes, colorants useful in visualizing the written  
30 image, and other addenda may be added to the hydrophilic layer, as long as their level is low enough that there is no significant interference with the ability of the layer to hold water and repel ink.

The laser used to expose the lithoplate of this invention is preferably a diode laser, because of the reliability and low maintenance of diode laser systems,  
35 but other lasers such as gas or solid state lasers may also be used.

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The layers are coated onto the support by any of the commonly known coating methods such as spin coating, knife coating, gravure coating, dip coating, or extrusion hopper coating. The process for using the resulting lithographic plate comprises the steps of 1) exposing the plate to a focused laser beam in the areas where ink is desired in the printing image, and 2) employing the plate on a printing press. No heating, post-imaging processing, or cleaning is needed before the printing operation. A vacuum dust collector may be useful during the laser exposure step to keep the focusing lens clean. Such a collector is fully described in US-A-5,574,493. The power, intensity and exposure level of the laser is fully described in the above cross referenced co-pending application..

The following examples illustrate the invention.

#### Example 1

A mixture of 10 g of carbon (Cabot Black Pearls 700) in 400 g methyl ethyl ketone and 400 g methylisobutyl ketone with 21 g of nitrocellulose was tumbled with 1 mm diameter zirconium oxide beads (the amount of beads filled half the container) for 24 hours. The beads were filtered off and the suspension was coated onto polyethylene terephthalate at  $32 \text{ cm}^3/\text{m}^2$  wet laydown. When dry, the web was overcoated with a solution of 120 g of colloidal silica stabilized with ammonia (Nalco 2326) mixed with 280 g of water, 2 g of aminopropyltriethoxysilane and 0.1 g of Zonyl FSN surfactant, the mixture coated at  $16 \text{ cm}^3/\text{m}^2$  wet laydown. The coating was dried for 3 minutes at  $118^\circ\text{C}$ . The coating was then exposed to a focused diode laser beam at 830 nm wavelength on an apparatus similar to that described in US-A-5,446,477. The exposure level was about  $600 \text{ mJ}/\text{cm}^2$ , and the intensity of the beam was about  $3 \text{ mW}/\mu^2$ . The laser beam was modulated to produce a halftone dot image. After exposure the plate was mounted on an ABDick press and several thousand good impressions were made.

#### Example 2

A mixture of tetrabutyltitanate in propanol was stirred with slow addition of a total of 5% water, added as 10% water in propanol. The tetrabutyltitanate amount was chosen so the total concentration was 0.5% after addition of the water in propanol. After 2 hours the mixture had a slightly hazy appearance. The mix was then coated at  $21.5 \text{ cm}^3/\text{m}^2$  on the carbon-nitrocellulose coated support of Example 1 and dried at  $118^\circ\text{C}$  for 3 minutes. The coating was



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then exposed to a focused diode laser beam at 830 nm wavelength on an apparatus similar to that described in U.S. Patent 5,446,477. The exposure level was about 600 mJ/cm<sup>2</sup>, and the intensity of the beam was about 3 mW/μ<sup>2</sup>. The laser beam was modulated to produce a halftone dot image. After exposure the plate was mounted on an ABDick press and several adequate impressions were made.

### Example 3

A mixture of 5% colloidal alumina (Dispal 18N4-20) with 0.5% hydrolyzed tetraethylorthosilicate (prepared by stirring together for 10 minutes 22 g tetraethylorthosilicate, 44 g water and 44 g ethanol with 300 mg concentrated hydrochloric acid) and 0.5% zonyl FSN surfactant in water was coated at 21.5 cm<sup>3</sup>/m<sup>2</sup> on the carbon-nitrocellulose coated support of Example 1 and dried at 118 °C for 3 minutes. The coating was then held at 100 °C for 1 hour. The coating was then exposed to a focused diode laser beam at 830 nm wavelength on an apparatus similar to that described in US-A-5,446,477. The exposure level was about 600 mJ/cm<sup>2</sup>, and the intensity of the beam was about 3mW/μ<sup>2</sup>. The laser beam was modulated to produce a halftone dot image. After exposure the plate was mounted on an ABDick press and several thousand good impressions were made.

### Example 4

A mixture of 22 g of tetraethylorthosilicate, 44 g water and 44 g ethanol with 300 mg concentrated hydrochloric acid was diluted with 4.4 liters of water and 0.5% zonyl FSN surfactant in water was added. The mixture was coated at 21.5 cm<sup>3</sup>/m<sup>2</sup> on the carbon-nitrocellulose coated support of Example 1 and dried at 118 °C for 3 minutes. The coating was then held at 100 °C for 1 hour. The coating was then exposed to a focused diode laser beam at 830 nm wavelength on an apparatus similar to that described in US-A-5,446,477. The exposure level was about 600 mJ/cm<sup>2</sup>, and the intensity of the beam was about 3 mW/μ<sup>2</sup>. The laser beam was modulated to produce a halftone dot image. After exposure the plate was mounted on an ABDick press and several good impressions were made.

### Example 5

A solution of 4 g of nitrocellulose and 2g of 2-{2-{2-Chloro-3-((1,3-dihydro-1,1,3-trimethyl-2H-benz(e)indol-2-ylidene)ethylidene)-1-

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cyclohexen-1yl}-ethenyl}-1,1,3-trimethyl-1H-benz{e}indolium 4-methylbenzenesulfonate in 200 ml of a 70:30 mixture of methylisobutyl ketone and ethanol was coated at  $32.69 \text{ cm}^3/\text{m}^2$  onto a polyethylene terephthalate support. When dry, the web was overcoated with a solution of 120 g of colloidal silica  
5 stabilized with ammonia (Nalco 2326) mixed with 280 g of water, 2 g of aminopropyltriethoxysilane and 0.1 g of Zonyl FSN surfactant, the mixture coated at  $16 \text{ cm}^3/\text{m}^2$  wet laydown. The coating was dried for 3 minutes at  $118^\circ\text{C}$ . The  
10 coating was then exposed to a focused diode laser beam at 830 nm wavelength on an apparatus similar to that described in US-A-5,446,477. The exposure level was about  $600 \text{ mJ}/\text{cm}^2$ , and the intensity of the beam was about  $3 \text{ mW}/\mu^2$ . The laser beam was modulated to produce a halftone dot image. After exposure the plate was mounted on an ABDick press and several thousand good impressions were made.

15 Example 6

Example 5 was repeated but the nitrocellulose was replaced with cellulose acetate propionate and the mixture was coated at  $18.88 \text{ g}/\text{m}^2$ .

Example 7

20 Example 6 was repeated but the cellulose acetate propionate was replaced with polyvinylacetate.

Example 8

25 Example 6 was repeated but the cellulose acetate propionate was replaced with a novolac resin.

Example 9

Example 6 was repeated but the cellulose acetate propionate was replaced with poly( $\alpha$ -cyanoacrylate) and the solvent was acetonitrile.

30

Example 10

A mixture of 3% zirconium butoxide in propanol was stirred with slow addition of a total of 5% water, added as 10% water in propanol. The zirconium butoxide amount was chosen so the total concentration was 1% after  
35 addition of the water in propanol. After 2 hours the mixture had a slightly hazy appearance. The mix was then coated at  $21.5 \text{ cm}^3/\text{m}^2$  on the carbon-nitrocellulose

coated support of Example 1 and dried at 118 °C for 3 minutes. The layer was then overcoated with a solution of 1.5% aminopropyl triethoxysilane in 50:50 propanol:water and dried at 118 °C for 3 minutes. The coating was then exposed to a focused diode laser beam at 830 nm wavelength on an apparatus similar to that described in US-A-5,446,477. The exposure level was about 600 mJ/cm<sup>2</sup>, and the intensity of the beam was about 3 mW/μ<sup>2</sup>. The laser beam was modulated to produce a halftone dot image. After exposure the plate was mounted on an ABDick press and several adequate impressions were made.

10 Example 11

Example 1 was repeated but the hardener used was a mixture of dimethyl dimethoxysilane and methyl trimethoxysilane sold as Z-6070 by the Dow Corning Company. Several hundred good impressions were printed.

15 Example 12

Example 11 was repeated but the hardener used was a glycidoxypropyltrimethoxysilane. Several hundred good impressions were printed.

Control 1

20 A solution of 5% colloidal Alumina (Dispal 18N4-20) in water was coated at 21.5 cm<sup>3</sup>/m<sup>2</sup> onto the same carbon-nitrocellulose coated support used in Example 1 and dried for 3 minutes at 118 °C. The coating was then exposed to a focused diode laser beam at 830 nm wavelength on an apparatus similar to that described in US-A-5,446,477. The exposure level was about 600 mJ/cm<sup>2</sup>, and the intensity of the beam was about 3 mW/μ<sup>2</sup>. The laser beam was modulated to produce a halftone dot image. After exposure the plate was mounted on an ABDick press and impressions were made. After about 20 impressions the background began to scum. After 100 impressions the image was ugly and unusable. This shows that the crosslinker is essential for good press performance.

30

Control 2

Example 1 was repeated in all respects except the aminopropyltriethoxysilane crosslinking agent was omitted. After exposure the plate was mounted on an ABDick press and impressions were made. The background never did go completely white, but there was a faint, low contrast image visible for a few impressions. After about 20 impressions the background

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was so dark that the image was essentially invisible. This control shows that the crosslinking agent is essential for good press performance.

### Control 3

- 5                   A mixture of 1.76% titanium dioxide, 3.4% poly(vinyl alcohol) (Scientific Products, 96% hydrolyzed) 1.69% hydrolyzed tetraethylorthosilicate (prepared by stirring together for 10 minutes 22 g tetraethylorthosilicate, 44 g water, 44 g ethanol and 30 mg concentrated hydrochloric acid) 0.22% nonylphenoxypolyglycidol (surfactant) was coated at  $21.5 \text{ cm}^3/\text{m}^2$  on the carbon-nitrocellulose coated support of Example 1 and dried at  $118^\circ\text{C}$  for 3 minutes. The coating was then held at  $100^\circ\text{C}$  for 1 hour. The coating was then exposed to a focused diode laser beam at 830 nm wavelength on an apparatus similar to that described in US-A-5,446,477. The exposure level was about  $600 \text{ mJ}/\text{cm}^2$ , and the intensity of the beam was about  $3 \text{ mW}/\text{m}^2$ . The laser beam was modulated to produce a halftone dot image. After exposure the plate was mounted on an ABDick press and impressions were made. The first three or four impressions gave a light but visible image. By the tenth impression full ink density was achieved but the background had scummed to the point that the image was unrecognizable. This control shows that the process and element described in WO 94/18005 are vastly inferior to the present invention.
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- 15
- 20

### Control 4

- A mixture of 1.5% aminopropyltriethoxysilane in water was coated onto the carbon containing layer of Example 1. After drying the coating was exposed as in Example 1 and mounted on the press. The plate took ink everywhere, and no good images were printed. This shows that both the hardener and the colloidal oxide (such as silica) are needed for good printing performance.
- 25

## CLAIMS:

1. A lithographic printing plate comprising:
  - a) a support web, and
  - b) a coextensive melanophilic photothermal conversion layer coated on the webthe printing plate characterized as further comprising a coextensive melanophobic layer comprising a crosslinked polymeric matrix containing a colloid of beryllium, magnesium, aluminum, silicon, gadolinium, germanium, arsenic, indium, tin, antimony, tellurium, lead, bismuth or a transition metal oxide.
2. The printing plate of Claim 1 wherein the support is a polyester film, or anodized aluminum.
3. The printing plate as claimed in either Claim 1 or 2 wherein the photothermal conversion layer comprises carbon dispersed in a cellulosic binder.
4. The printing plate as claimed in any of Claims 1 to 3 wherein the melanophobic layer comprises carbon dispersed in nitrocellulose.
5. The printing plate as claimed in any of Claims 1 to 4 wherein the thickness of the melanophobic layer is from 0.05 to 1  $\mu\text{m}$ .
6. The printing plate as claimed in any of Claims 1 to 5 wherein the melanophobic layer contains less than 5% hydrocarbon groups by weight.
7. The printing plate as claimed in any of Claims 1 to 6 wherein the colloid is hydroxysilicon.
8. The printing plate as claimed in any of Claims 1 to 6 wherein the colloid is hydroxyaluminum, hydroxytitanium, or hydroxyzirconium.
9. The printing plate as claimed in any of Claims 1 to 6 wherein the crosslinked polymeric matrix is derived from a di-, tri or tetraalkoxy silane, titanate, zirconate or aluminate.

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10. A method of imaging comprising imagewise exposing a printing plate as claimed in any of Claims 1 to 9, to infrared irradiation to provide an image in exposed areas without post-imaging processing.

# INTERNATIONAL SEARCH REPORT

Inter. onal Application No

PCT/US 98/04638

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B41C1/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B41C G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 18005 A (AGFA GEVAERT NV ;VERBURGH YVES (BE); BERGH RUDOLF VAN DEN (BE); ME) 18 August 1994 cited in the application see page 7, line 11; claims	1
A	US 3 964 906 A (KENNEY JOHN THOMAS) 22 June 1976 see the whole document	1
A	DE 44 42 235 A (ROLAND MAN DRUCKMASCH) 8 June 1995 see the whole document	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

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